Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Photoinduced electron- and energy-transfer processes of [60]fullerene covalently bonded with one and two zinc porphyrin(s): Effects of coordination of pyridine and diazabicyclooctane to Zn atom

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Contents:

Steady state absorption and fluorescence spectra, fluorescence time profiles, transient absorption spectra in the presence and absence of Py and DABCO, and experimental details.

(Figures S1 ~ S14, and Syntheses of **2, 3, 6, 7, 9** and **10**)

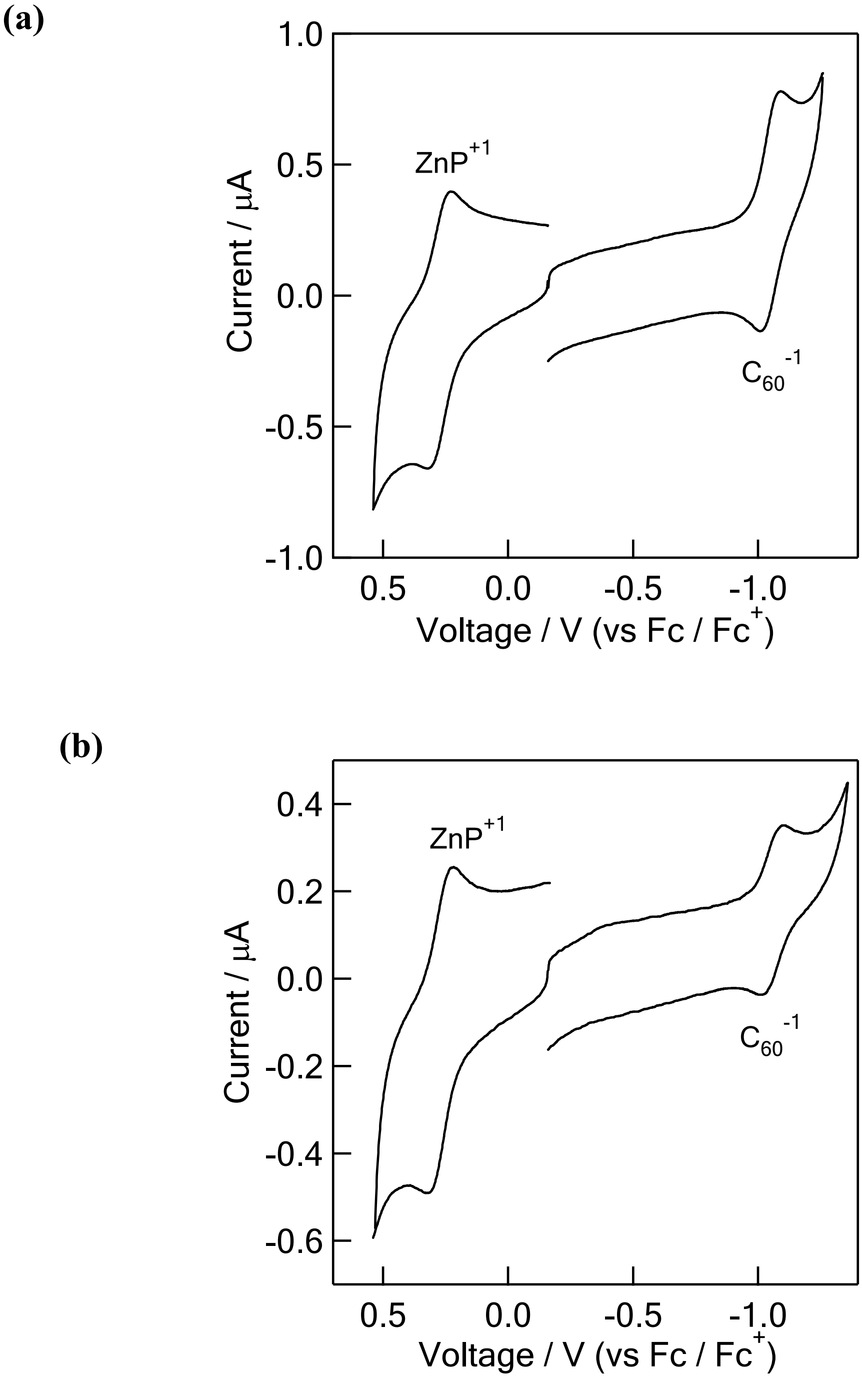


Fig. S1 Cyclic voltammograms of (a) **ZnP-C_{60}** (0.1 mmol dm^{-3}) and (b) **ZnP-C_{60}-ZnP** (0.1 mmol dm^{-3}) in the presence of *n*-Bu_4NPF_6. (0.1 mol dm^{-3}) in PhCN. Scan rate = 100 mV s^{-1}.

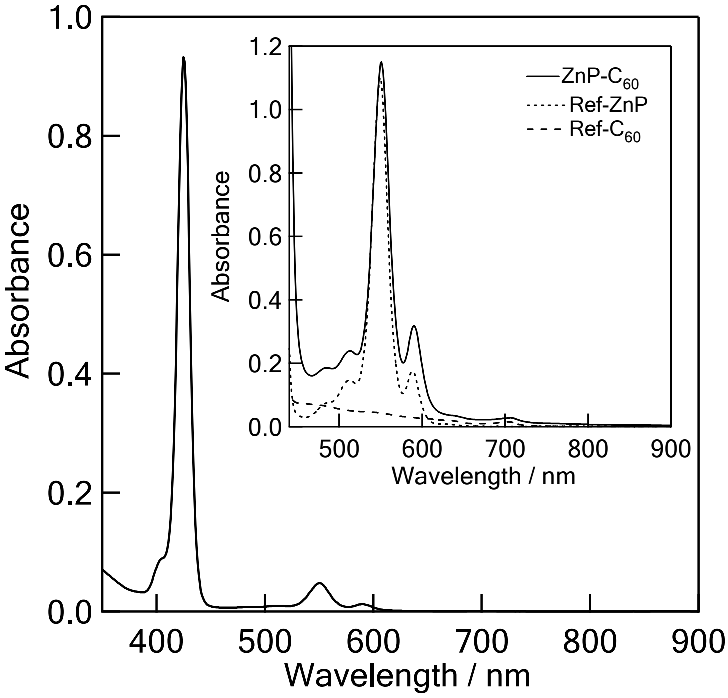


Fig. S2 Steady-state absorption spectra of **ZnP-C$_{60}$** (0.005 mmol dm^{-3}) in toluene. Inset: Steady-state absorption spectra of **ZnP-C$_{60}$** (0.1 mmol dm^{-3}) with reference compounds **ZnP** and **C$_{60}$** in the same concentration in toluene.

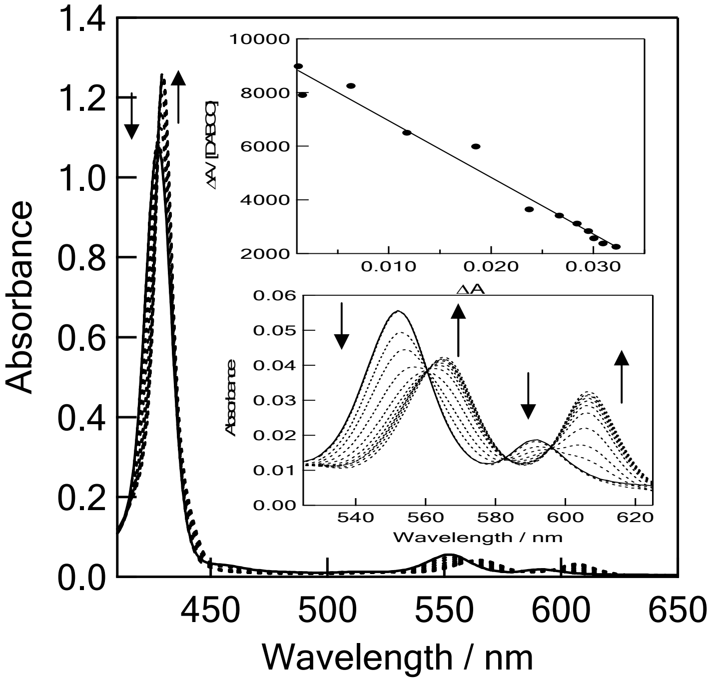


Fig. S3 Steady-state absorption spectral changes observed by the titration of **ZnP-C$_{60}$-ZnP** (0.05 mmol dm^{-3}) with **DABCO** (step = 0.05 mmol dm^{-3}) in *o*-DCB. Inset: Scatchard plots at 552 nm. Arrows imply the direction of changes with increasing [DABCO].

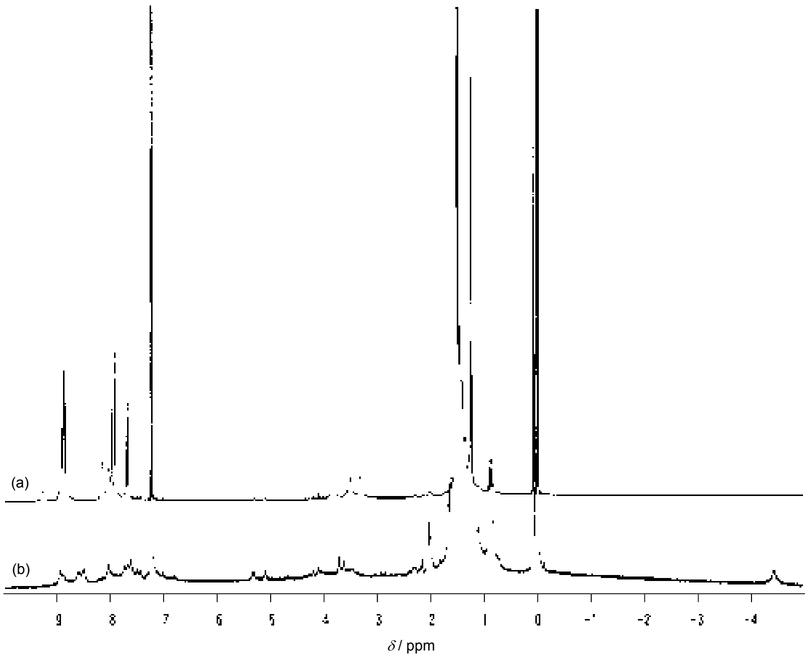


Fig. S4 ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectra of **ZnP-C60-ZnP** (2.8 mmol dm^{-3}) (a) before and (b) after addition of 1 equiv of DABCO.

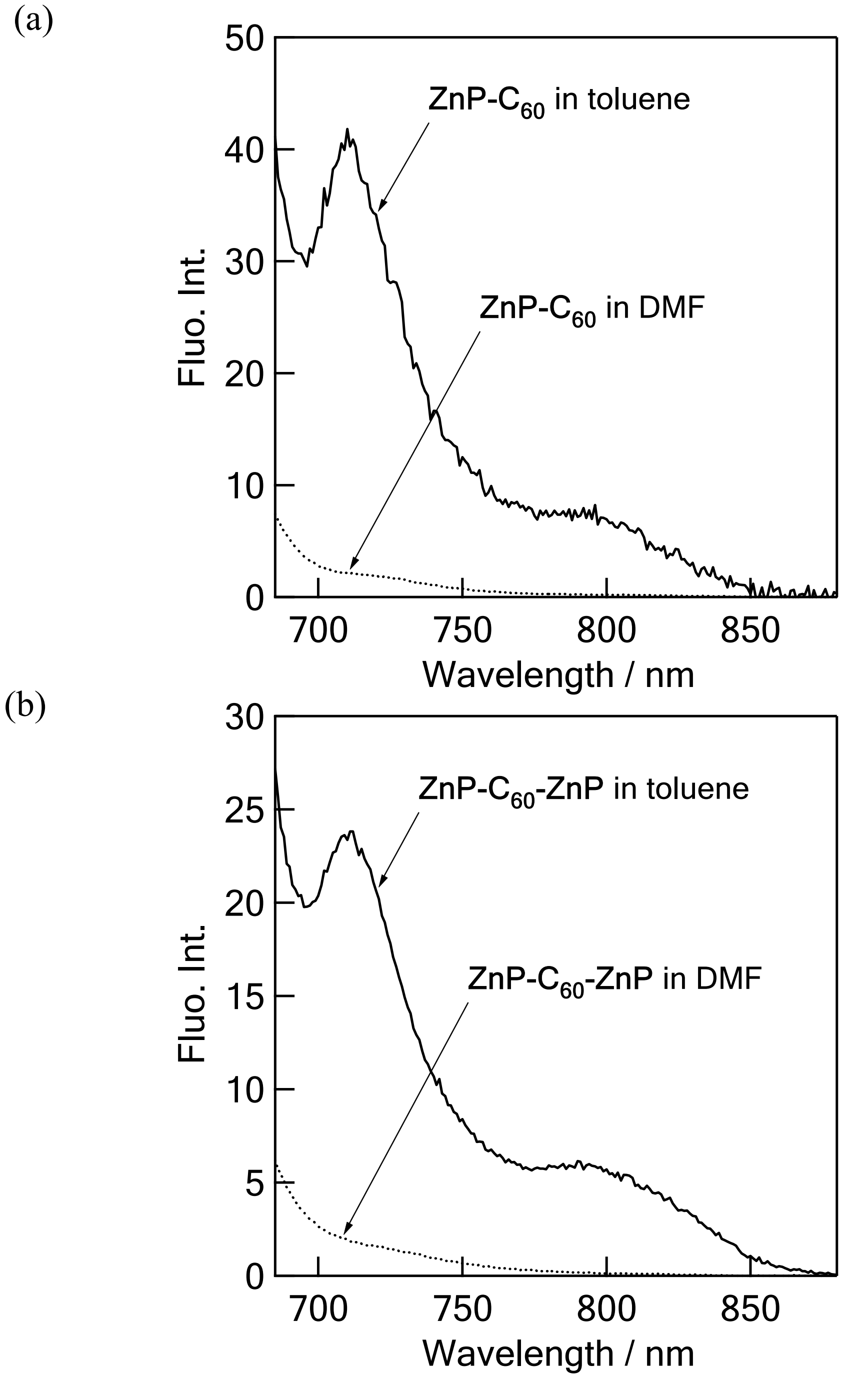


Fig. S5 Steady-state fluorescence spectra of (a) **ZnP-C_{60}** (b) **ZnP-C_{60}-ZnP** (0.1 mmol dm^{-3}) in toluene (λ_{ex} = 640 nm).

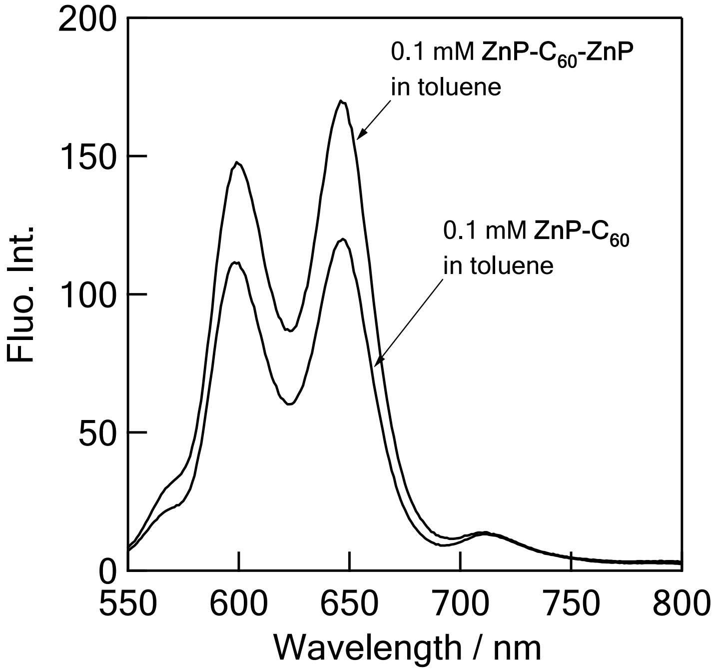


Fig. S6 Comparison of steady-state fluorescence intensities between **ZnP-C_{60}** (0.1 mmol dm^{-3}) and **ZnP-C_{60}-ZnP** (0.1 mmol dm^{-3}) in toluene (λ_{ex} = 550 nm).

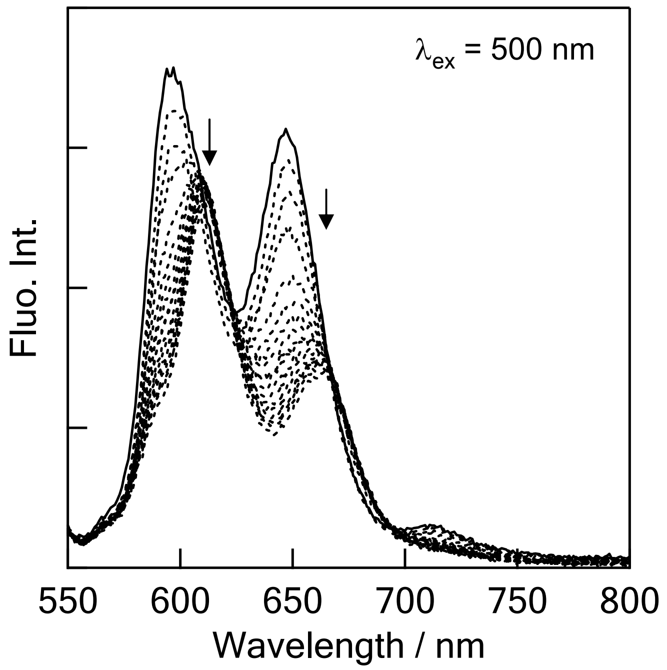


Fig. S7 Steady-state fluorescence Spectral changes observed by the titration of **ZnP-C_{60}-ZnP** (0.05 mmol dm^{-3}) with Py (step = 0.001 mmol dm^{-3}) in toluene (λ_{ex} = 500 nm) Arrows imply the direction of changes with increasing [DABCO].

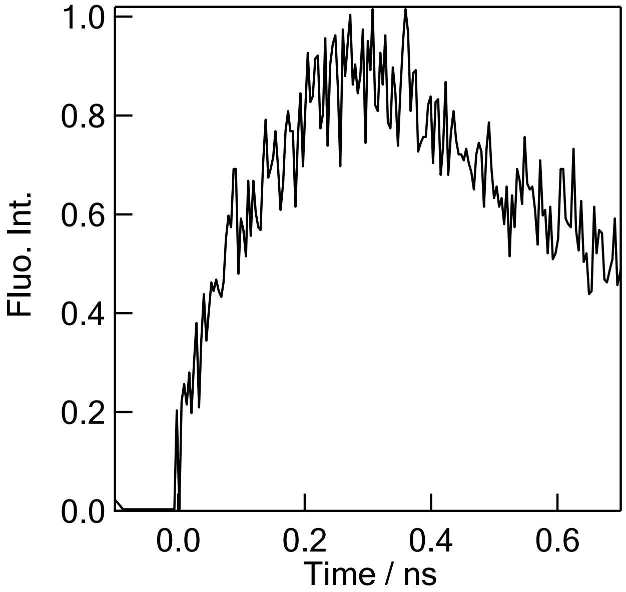


Fig. S8 Time profile of the fluorescence at 720 nm of **ZnP-C_{60}** in toluene. Excitation wavelength was 410 nm.

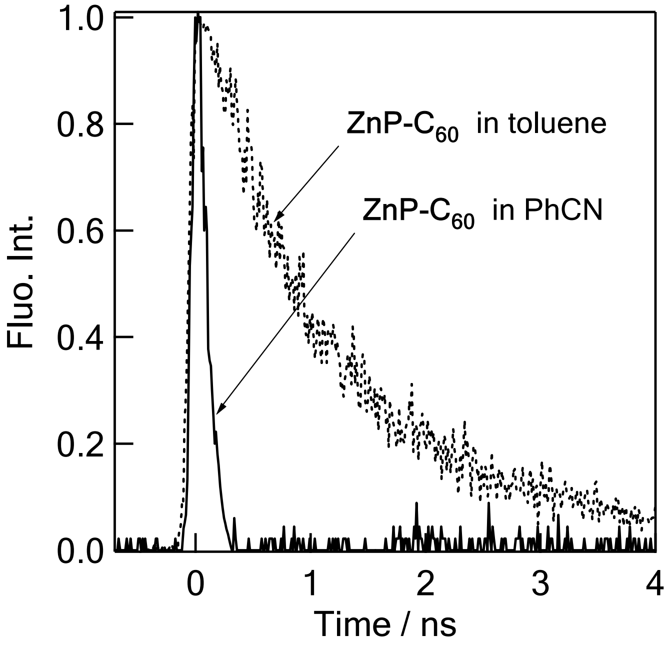


Fig. S9 Time profiles of the fluorescence at 720 nm of **ZnP-C_{60}** in PhCN and toluene. Excitation wavelength was 410 nm.

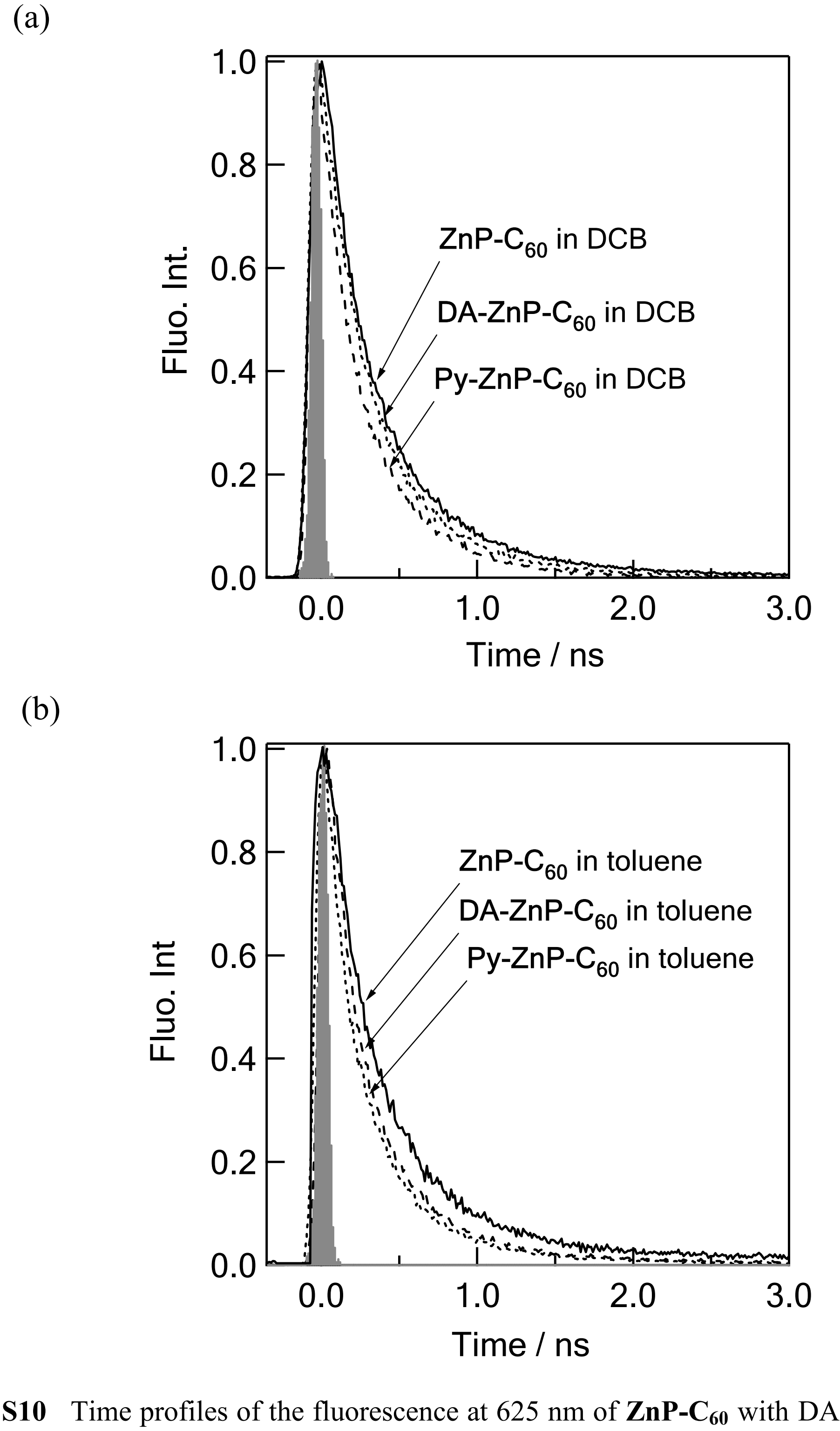


Fig. S10 Time profiles of the fluorescence at 625 nm of **ZnP-C_{60}** with DABCO and Py (a) in *o*-DCB (= DCB) and (b) in toluene. Excitation wavelength was 410 nm.

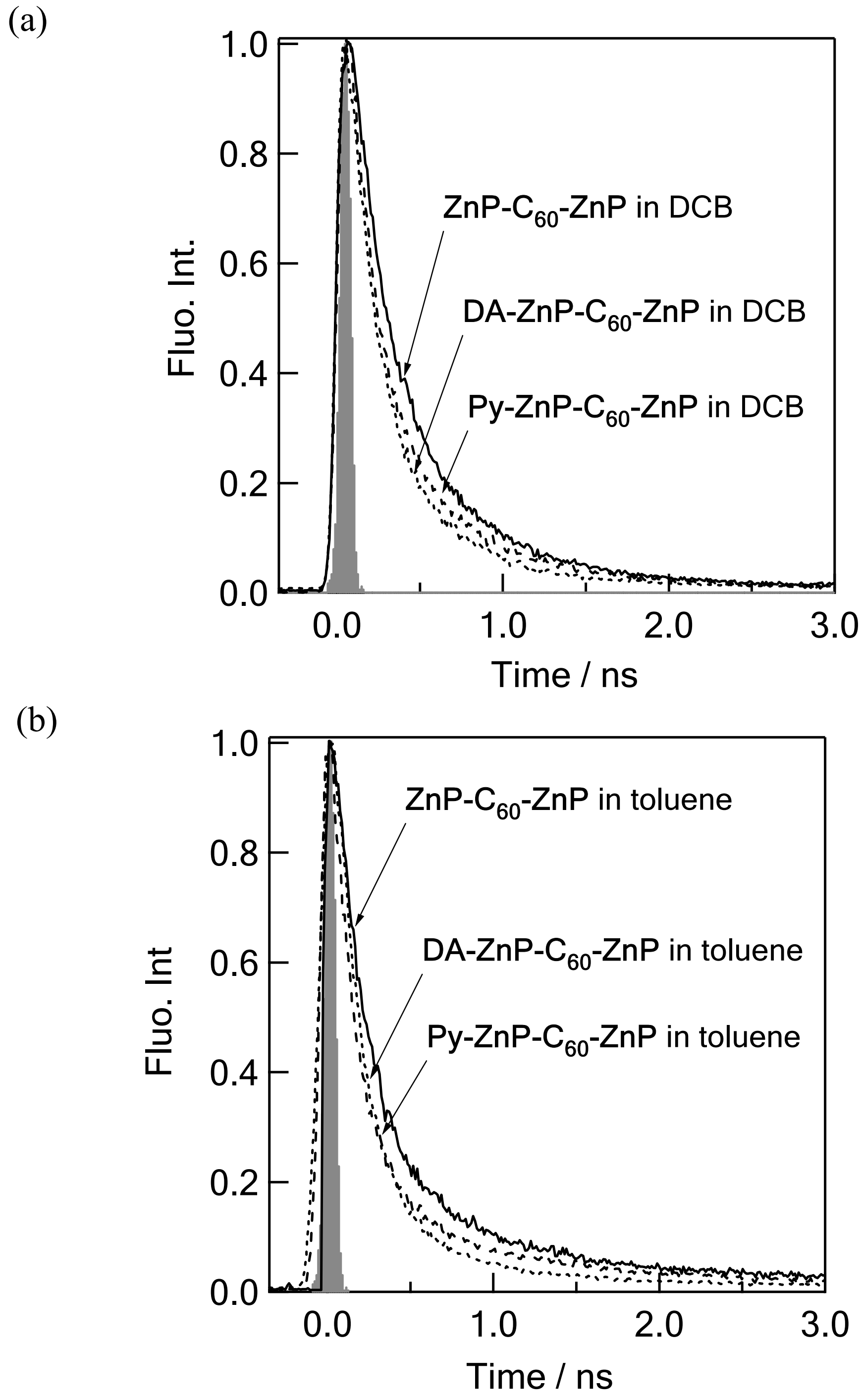


Fig. S11 Time profiles of the fluorescence at 625 nm of **ZnP-C_{60}-ZnP** with DABCO and Py (a) in *o*-DCB (= DCB) and (b) in toluene. Excitation wavelength was 410 nm.

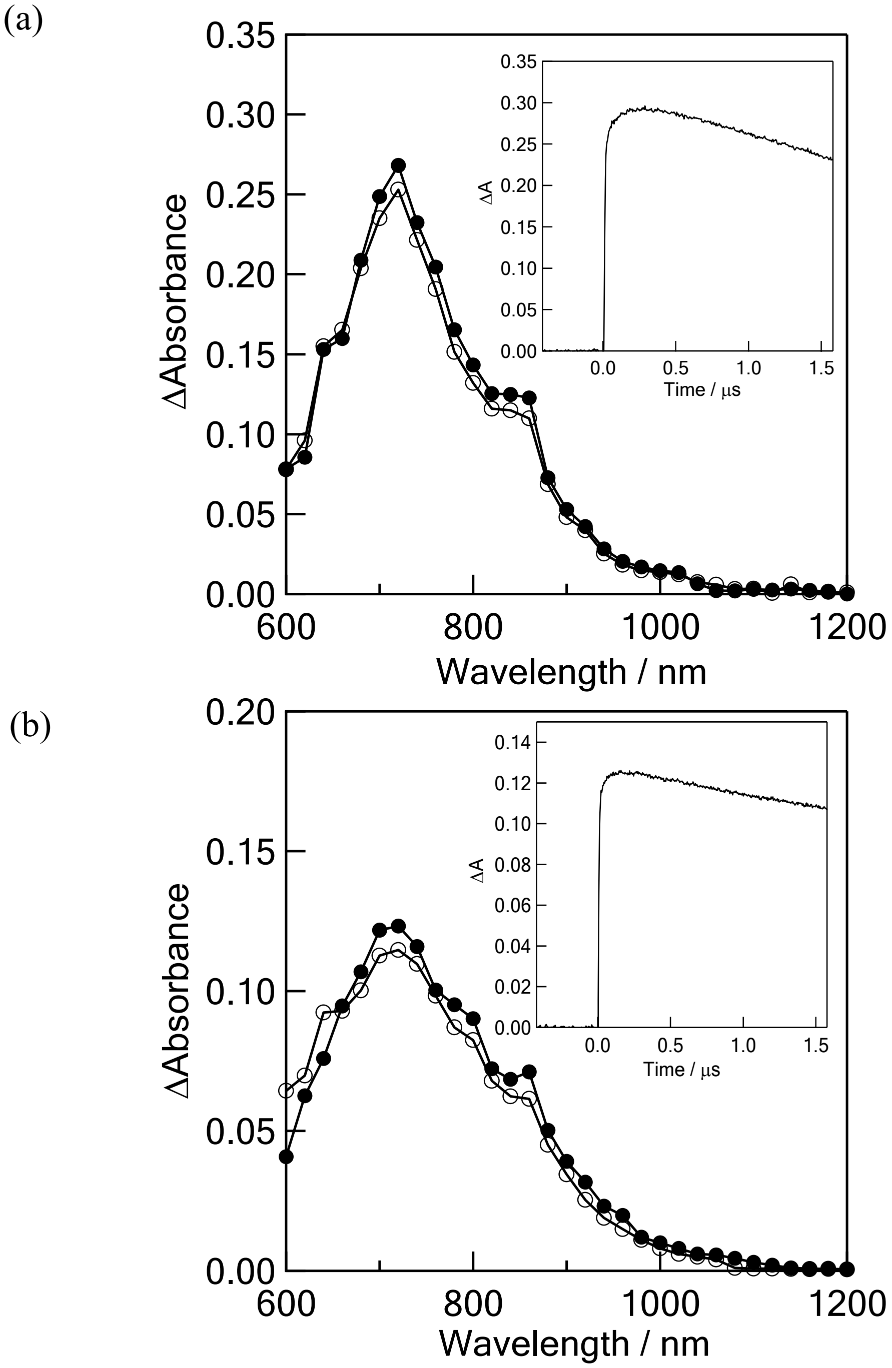


Fig. S12 Nanosecond transient absorption spectra of and (a) **ZnP-C$_{60}$** (b) **ZnP-C$_{60}$-ZnP** (0.1 mmol dm^{-3}) observed by 532 nm laser irradiation in at 0.1 μs (●) and 1.0 μs (○) in Ar-saturated toluene. Inset: Absorption-time profiles at 720 nm in toluene.

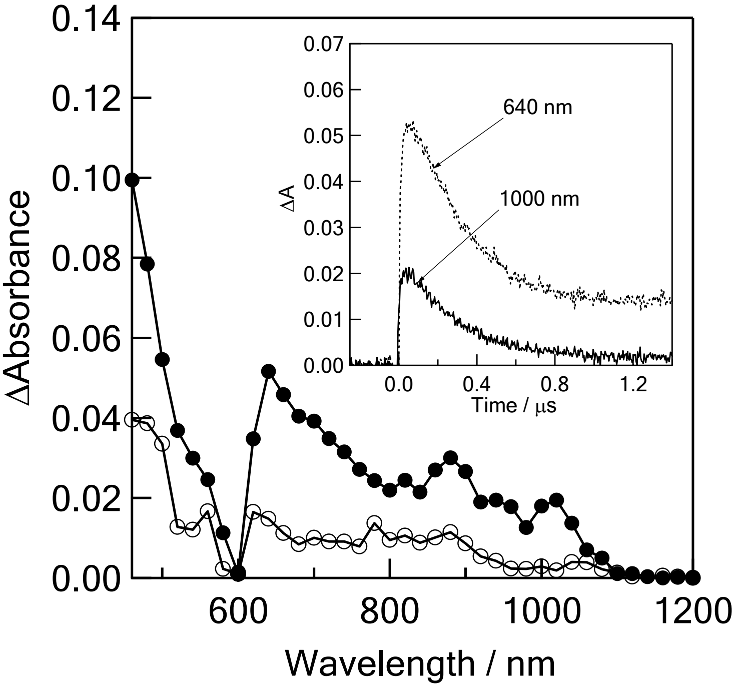


Fig. 11 Nanosecond transient absorption spectra of **ZnP-C_{60}-ZnP** (0.1 mmol dm^{-3}) observed by 532 nm laser irradiation in at 0.1 μs (●) and 1.0 μs (○) in Ar-saturated PhCN. Inset: Absorption-time profiles in PhCN.

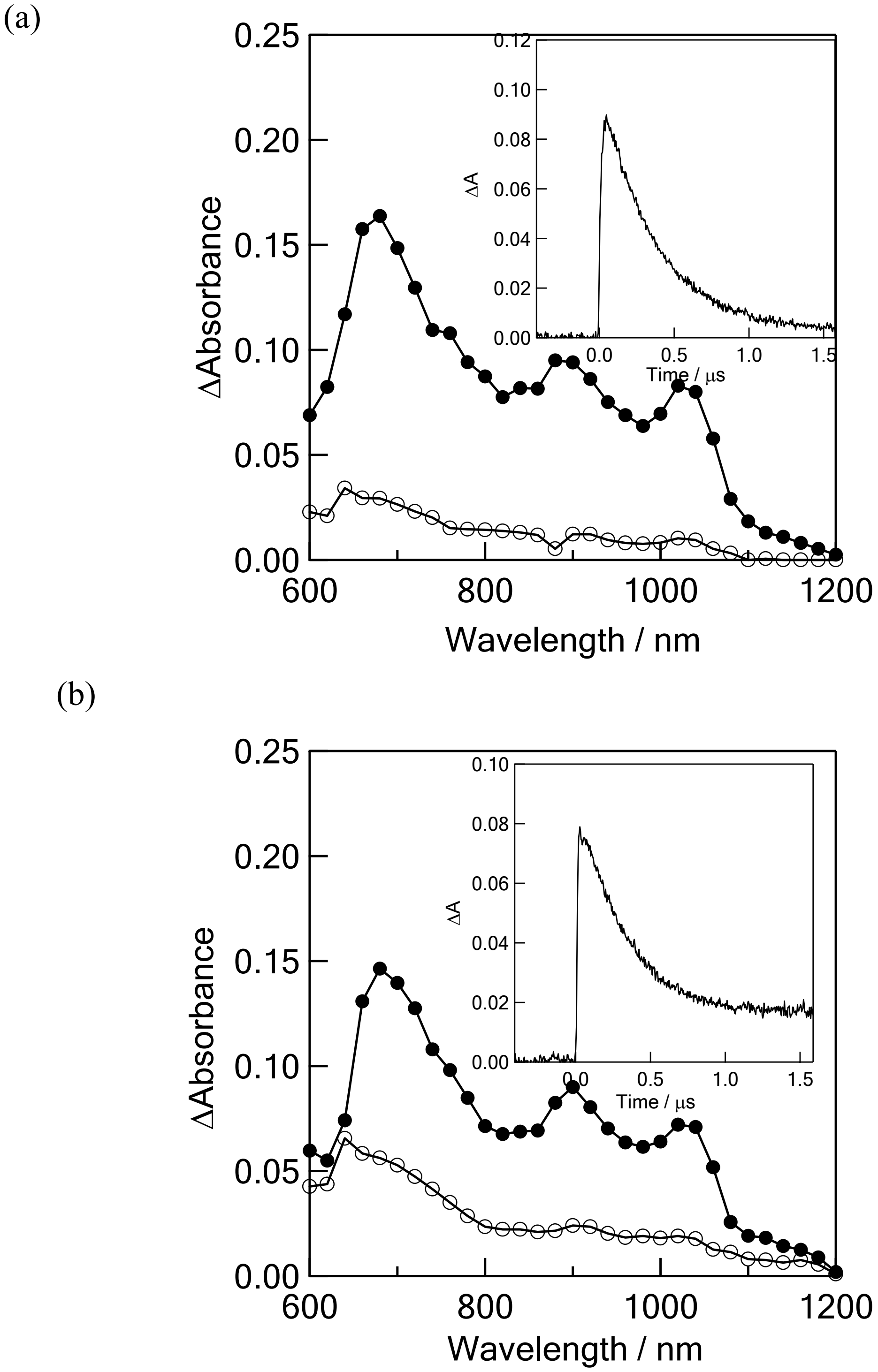


Fig. S12 Nanosecond transient absorption spectra of (a) (0.1 mmol dm^{-3}) **ZnP-C$_{60}$** with Py (0.1 mmol dm^{-3}) and (b) **ZnP-C$_{60}$-ZnP** (0.1 mmol dm^{-3}) with Py (0.2 mmol dm^{-3}) observed by 532 nm laser irradiation in at 0.1 μs (●) and 1.0 μs (○) in Ar-saturated *o*-DCB. Inset: Absorption-time profiles at 1020 nm in Ar-saturated *o*-DCB.

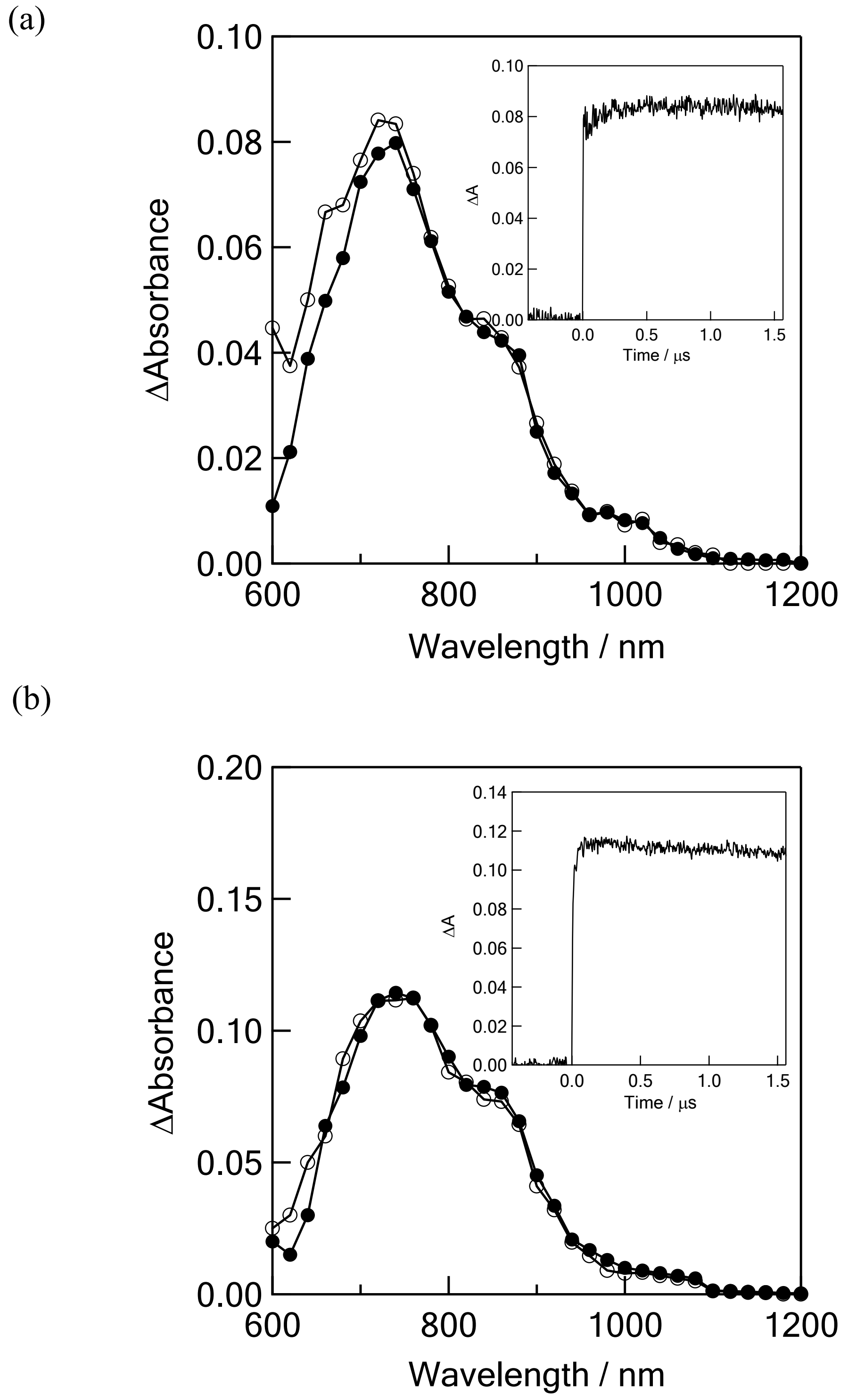
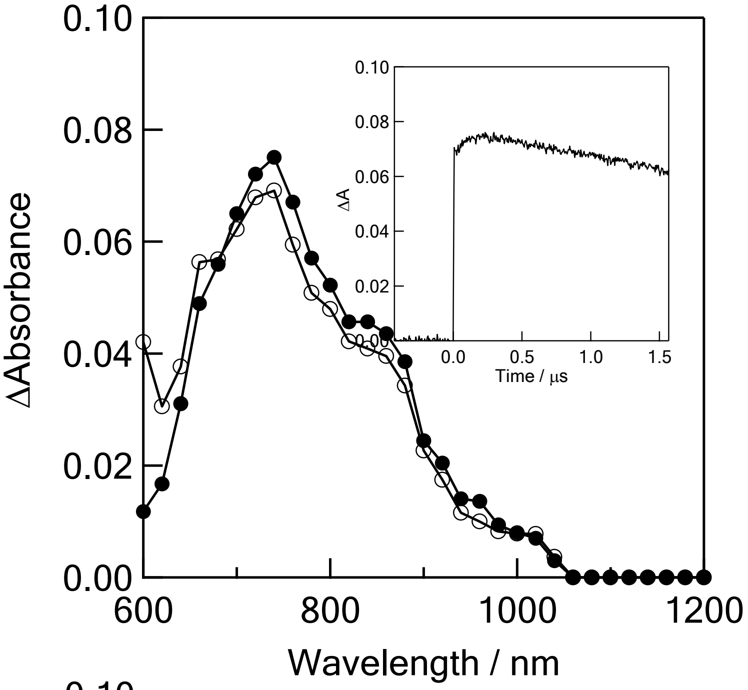


Fig. S13 Nanosecond transient absorption spectra of (a) **ZnP-C$_{60}$** (0.07 mmol dm^{-3}) with **DABCO** (0.07 mmol dm^{-3}) and (b) **ZnP-C$_{60}$-ZnP** (0.1 mmol dm^{-3}) with DABCO (0.1 mmol dm^{-3}) observed by 532 nm laser irradiation in at 0.1 μs (●) and 1.0 μs (○) in Ar-saturated toluene. Inset: Absorption-time profiles at 720 nm in toluene.

(a)



(b)

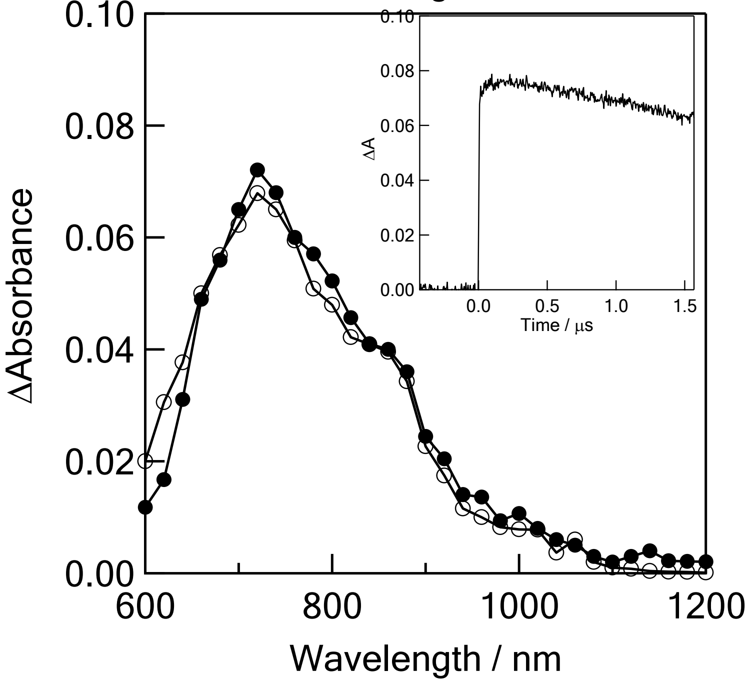


Fig. S14 Nanosecond transient absorption spectra of (a) **ZnP-C$_{60}$** (0.06 mmol dm^{-3}) with Py (0.06 mmol dm^{-3}) and (b) **ZnP-C$_{60}$-ZnP** (0.08 mmol dm^{-3}) with Py (0.16 mmol dm^{-3}) observed by 532 nm laser irradiation in at 0.1 μs (●) and 1.0 μs (○) in Ar-saturated toluene. Inset: Absorption-time profiles at 720 nm in toluene.

Experimental Details:

Synthesis of 2. To a tetrahydrofuran/methanol (12.0 mL/5.40 mL) solution of **1** (2.57 g, 12.2 mmol) was added a methanol (9.10 mL) solution of a mixture of methyl thioglycolate (1.25 mL, 14.0 mmol) and triethylamine (2.10 mL, 15.1 mmol). The mixture was stirred at room temperature overnight, and evaporated to dryness. The residue was separated by silica gel chromatography (chloroform/ethyl acetate/hexane = 3/2/2, R*f* = 0.33) to afford **2** (2.30 g, 9.73 mmol, 80%) as a colorless crystal. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.95 (t, *J* = 1.2 Hz, 1H), 3.87-3.86 (m, 4H), 3.75 (s, 3H), 3.40 (s, 2H), 3.15 (s, 2H) ppm; IR (KBr) 1732, 1307, 1242, 1120 cm^{-1}.

Synthesis of 3. A mixture of **2** (1.95 g, 8.26 mmol) with 6 M HCl was stirred at 60 °C overnight. After cooling, precipitated crystal (**3**, 1.09 g, 4.92 mmol, 60%) was collected by filtration as a white powder. Since **3** was analytically pure enough, it was used without further purification. m.p. 95 - 97 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.95 (s, 1H), 3.87 (s, 4H), 3.42 (s, 2H), 3.20 (s, 2H) ppm; IR (KBr) 1701, 1325, 1205, 1146 cm^{-1}.

Synthesis of 6. A mixture of **3** (44.4 mg, 0.200 mmol), oxalyl chloride (70.0 µL, 0.802 mmol), and *N,N*-dimethylformamide (1 drop) was stirred in chloroform (1.00 mL) at room temperature for 1 h. The resulting yellow solution was concentrated in vacuo. The residual oil was dissolved in chloroform (2.00 mL), and added to a chloroform (6.00 mL) solution of a mixture of **5** (248 mg, 0.257 mmol) and triethylamine (40.0 µL, 0.287 mmol). The mixture was stirred at room temperature overnight and evaporated to dryness. The residue was chromatographed on silica gel (chloroform, *Rf* = 0.13) and the crude product was purified by preparative HPLC to afford **6** (81.8 mg, 69.9 µmol, 35%) as a purple solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.06-8.96 (m, 9H), 8.30-8.22 (m, 8H), 7.92-7.83 (m, 5H), 5.93 (s, 1H), 3.87-3.86 (m, 4H), 3.34 (s, 2H), 3.25 (s, 2H), 1.65 (s, 54H), -2.54 (s, 2H) ppm; IR (KBr) 3414, 2960, 1593, 1522, 1318, 1245 cm^{-1}; FAB-MS (matrix : mNBA) m/z 1106 $[M-SO_2]^+$.

Synthesis of 7: A mixture of fullerene (C_{60}, 187 mg, 259 μmol), **6** (75.5 mg, 64.5 μmol), and hydroquinone (1.00 mg, 9.08 μmol) was refluxed in 1,2-dichlorobenzene (10.0 mL) for 4 h. The reaction mixture was evaporated to dryness. The residue was chromatographed on silica gel (toluene/ethyl acetate = 47/3, *Rf* = 0.56) to give crude product which was purified by preparative HPLC to afford **7** (47.8 mg, 26.2 μmol, 41%) as a black purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.85-8.81 (m, 8H), 8.19 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 8.06-8.00 (m, 6H), 7.80-7.79 (m, 3H), 6.60 (t, *J* = 4.8 Hz, 1H), 3.73 (s, 2H), 3.60 (s, 2H), 3.28 (s, 2H), 3.21 (s, 2H), 1.55 (s, 18H), 1.52 (s, 36H), -2.85 (s, 2H) ppm; IR (KBr) 2961, 1591, 1517, 1474, 1362, 1247, 801 cm^{-1}; FAB-MS (matrix : mNBA) m/z 1827 $[M+H]^+$.

Synthesis of 9. Title compound **9** was synthesized from **8** by a similar procedure to that of **6**. **9** was obtained (57%) as a purple solid. m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 3.2 Hz, 16H), 8.66 (s, 2H), 8.25 (d, *J* = 8.2 Hz, 4H), 8.06 (t, *J* = 1.9 Hz, 12H), 8.01 (d, *J* = 8.2 Hz, 4H), 7.78 (t, *J* = 1.9 Hz, 2H), 7.76 (t, *J* = 1.9 Hz, 4H), 4.16 (s, 4H), 3.74 (s, 4H), 3.56 (s, 4H), 1.51 (s, 36H), 1.49 (s, 72H), -2.72 (s, 4H) ppm; IR (KBr) 2960, 1592 cm^{-1}; FAB-MS (matrix : mNBA) m/z 2159 $[M+H-SO_2]^+$.

Synthesis of 10. Title compound **10** was synthesized from **9** by a similar procedure to that of **7**. **10** was obtained (16%) as a black purple solid. m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 2H), 8.85-8.78 (m, 16H), 8.20 (d, *J* = 8.0 Hz, 4H), 7.11 (ddd, *J* = 1.2 Hz and 2.7 Hz and 8.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 4H), 4.18 (t, *J* = 4.8 Hz, 4H), 3.88 (t, *J*

= 4.8 Hz, 4H), 3.77 (s, 4H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm; IR (KBr) 3437, 2959, 1593, 1514, 1247, 801 cm^{-1}.